Missouri Department of Natural Resources
Water Protection Program

Total Maximum Daily Load (TMDL)

for

McKenzie Creek
Wayne County, Missouri

Completed: October 7, 2004
Approved : November 15, 2004

Total Maximum Daily Load (TMDL)
For McKenzie Creek
Pollutant: pH

State map showing location of watershed

Name: McKenzieCreek

Location: Near Piedmont in Wayne County, Missouri

Hydrologic Unit Code (HUC): 11010007 - 060001

Water Body Identification Number (WBID): 2787

Missouri Stream Class: Class C stream[1]

Beneficial Uses:
- Livestock and Wildlife Watering
- Protection of Warm Water Aquatic Life
- Protection of Human Health associated with Fish Consumption

Size of Impaired Segment: 0.5 mile

Location of Impaired Segment: From NW ¼ Section 3, T29N, R3E (downstream) to SW ¼ Section 34, T30N, R3E (upstream)

Pollutant: pH

Pollutant Source: Natural[2]

TMDL Priority Ranking: Medium

1. Background and Water Quality Problems

Area History:[3]

The earliest recorded date of a permanent settlement in what is now Wayne County is 1801. At that time, Joseph Parish, from Virginia, settled on Clark's Creek with his wife and seven children, not far from the St. Francis River near Patterson.

Over two and one-half years before Missouri became a state, the last territorial assembly took land from Cape Girardeau and Lawrence counties to form Wayne County. It was organized Dec. 11, 1818, (effective Feb. 1, 1819). Popularly known as the State of Wayne, the county covered most of

[1] Class C streams may cease to flow in dry periods but maintain permanent pools that support aquatic life. See 10 CSR 20-7.031(1)(F)
[2] While the pollutant source is listed as "natural" in the 2002 303(d) list, this document suggests that atmospheric deposition/acid rain is the most likely source of acidity in McKenzie Creek.
[3] A Pictorial History of Wayne County, Missouri. Mother of Southern Missouri Counties. 1992. Wayne County Journal – Banner. Howard Ellinghouse and Mary Beth Stivers, publishers.

the southern quarter of Missouri. It stretched west from Cape Girardeau and New Madrid counties to Missouri's western border, and south to Arkansas. Starting in 1831, 24 whole counties and parts of eight others were carved from Wayne County, leading to its other nickname, the Mother of Southern Missouri Counties.

The county was named for General Anthony Wayne of the American Revolutionary War. The county seat was named Greenville in honor of the Treaty of Greenville, signed between Gen. Wayne and the Miami Indians in 1794 after the Battle of Fallen Timbers near Toledo, Ohio. This treaty opened the Northwest Territory to American settlers. For many years Greenville was the only village in the county. Goods were hauled by wagon from Ste. Genevieve, and it was not until 1830 that the government made provision to have mail carried to the town. Greenville's site on the St. Francis River was prone to floods. The worst one was on August 26, 1915, when there was five feet of water in the streets. Over 20 years later, in 1936, Congress signed the Overton Act, also called the Flood Control Act. This Act included the St. Francis [River] Basin Project and construction of Lake Wappapello, which was completed in 1941. At that time the town was moved to higher ground, but fewer than half of the residents moved to the new location.

The first to settle in the area of Piedmont on McKenzie Creek were two brothers from Alabama, James and William Daniel. In 1860, the town was called Danielsville. Then in 1871 the Iron Mountain Railroad arrived and, because it owned so much of the town and surrounding land, the railroad changed the name of Danielsville to Piedmont. Piedmont means "at the base of the mountain" and refers to the fact that the town sits just south of Charles Mountain, one of Missouri's highest points at 1,452 feet.

Soils and Land Use:
"From the highest granite knobs of the northwest, the elevation above sea level rushes downward to Mingo Swamp below Wappapello Lake."[4] At most places in Missouri, igneous rocks are at least one half mile below the ground surface, but the mountains of northern Wayne County are exposed igneous knobs. Further south the soil is weathered limestone, which was laid down in an ancient inland sea. Three rivers flow across Wayne County in a southeasterly direction, the Castor River on the east, the St. Francis down the middle and the Black on the western side. Before modern flood control, the three rivers would become one during major floods. McKenzie Creek is a tributary to the Black River, draining the northwest corner of the county. Upper McKenzie Creek flows across the following soils. The Clarksville-Scholten complex is a very gravelly silt loam with 15 to 45 percent slopes that is very deep and moderately well drained. It is very stony and found on backslopes. Irondale is a gravelly silt loam of 15 to 35 percent slope, moderately deep, rocky and extremely bouldery. It is a well drained soil whose parent material is residuum weathered from rhyolite. The Tilk-Secesh complex is a silt loam that is deep and moderately well drained with a zero to three- percent slope. Tilk is found in the high flood plain while Secesh makes up the low stream terrace. A discussion about the possibility of acidity from this soil complex may be found in the Source Analysis section under Buffering Capacity.

The land is primarily used for forest/woodlands (86 percent) and grasslands (11 percent). There are no towns in the watershed above the impaired section. More detailed land use information may be found in Appendix A.

[4] Cramer, Rose Fulton. Wayne County, Missouri. 1972. The Ramfre Press, Cape Girardeau, MO

Defining the Problem:
In the upper portion of its watershed, a one-half mile segment of McKenzie Creek is impaired by low (acidic) pH, due primarily to the acidic rainwater and the predominance of igneous rock in the area. Rainwater in this area averages a pH of 4.90 SU. Table 1 shows the median pH was 4.64 SU in 2001. Igneous rock (granite and rhyolite, in this case) is unable to buffer the low pH of this rainwater. Limestone on the other hand, which is abundant in most of Missouri but lacking in this area, is composed of calcium carbonate and is a good buffer. Missouri Water Quality Standards (WQS) require the pH of state waters to be between 6.5 and 9.0 SU.

- **Source Analysis: Point Sources**

The only permitted point source within the watershed upstream from the impaired segment is Gad's Hill Quarry, which is managed by GS Roofing Products Company (Permit number MO-0110051). The quarry produces crushed granite for railroad beds and shingles and was listed on the 1998 303(d) list as the source of the low pH in the creek. However, data collected between 1992 and 2003 shows that pH values upstream of the quarry and two miles downstream of the quarry are similar and are too low to meet state standards. Three and a half miles below the quarry a pH of 6.4 SU (lower than WQS) was recorded in 1992, however all values at that site since that time have ranged between 7.1 and 7.9 (well within WQS). Maps of the sampling sites are in Appendix B and the data are in Appendix C.

On April 16, 2001, DNR issued a notice of violation (NOV) to the quarry for non-compliance with its permit requirement. Effluent (discharge) from all outfalls had low pH readings, in particular outfalls #001 and #002 (3.21 and 3.7 respectively)[5]. Then in August 2001, the operators of the quarry started applying caustic (very alkaline) treatment to control acidity (McGee, 2004). During an inspection of the facility on February 6, 2003, DNR staff took pH readings 30 yards upstream and 300 yards downstream of the confluence of the unclassified receiving stream and McKenzie Creek. At the downstream site, the pH was 7.1. At Outfall #001, the pH was 6.8. But *up*stream, the pH was 6.4 (Chronister, 2004). This is an indication that there are other sources contributing to the acidity in McKenzie Creek.

- **Source Analysis: Nonpoint Source Component**

There are no permitted concentrated animal feeding operations within the watershed upstream of the impaired length of McKenzie Creek and about 12 percent of the watershed is in pasture. Hay production and pasture management are improbable significant nonpoint sources of stream acidity.

Following discussions with personnel from the department's Southeast Regional Office and the Missouri Department of Conservation, no significant anthropogenic source of stream acidity in the watershed could be identified (Blatz, 2004; Chronister, 2004). A survey of the watershed in March of 2004 revealed a small logging operation on private property at the edge of the watershed. However, pH measurements in McKenzie Creek upstream of the drainage point from the logged area were also acidic. The survey did not reveal any other management practices that might be contributing to acidity in the creek.

Atmospheric Deposition

Atmospheric deposition is most likely the source of stream acidity in McKenzie Creek. Acid rain in Missouri is not normally considered to be an issue of the same magnitude as it is in the

[5] See Appendix B-2 for a map of the outfalls.

northeastern United States, where there are no carbonate rocks to buffer it. Normal rain pH is around 5.5 (EPA, 2003; USGS, 1997). However, data from the National Atmospheric Deposition Program (NADP) National Trends Network (NTN) indicate that acid rain is a significant factor in southeastern Missouri. The following summary statistics are derived from data from the monitoring station at the University of Missouri Forestry Camp, located about 30 miles southeast of McKenzie Creek. This shows a median pH of 4.6 and an average of 4.7 SU.

Table 1: Summary statistics of precipitation pH at NADP/NTN Monitoring Location MO05, University Forest, Butler County, MO 1992-2003. (407 samples)

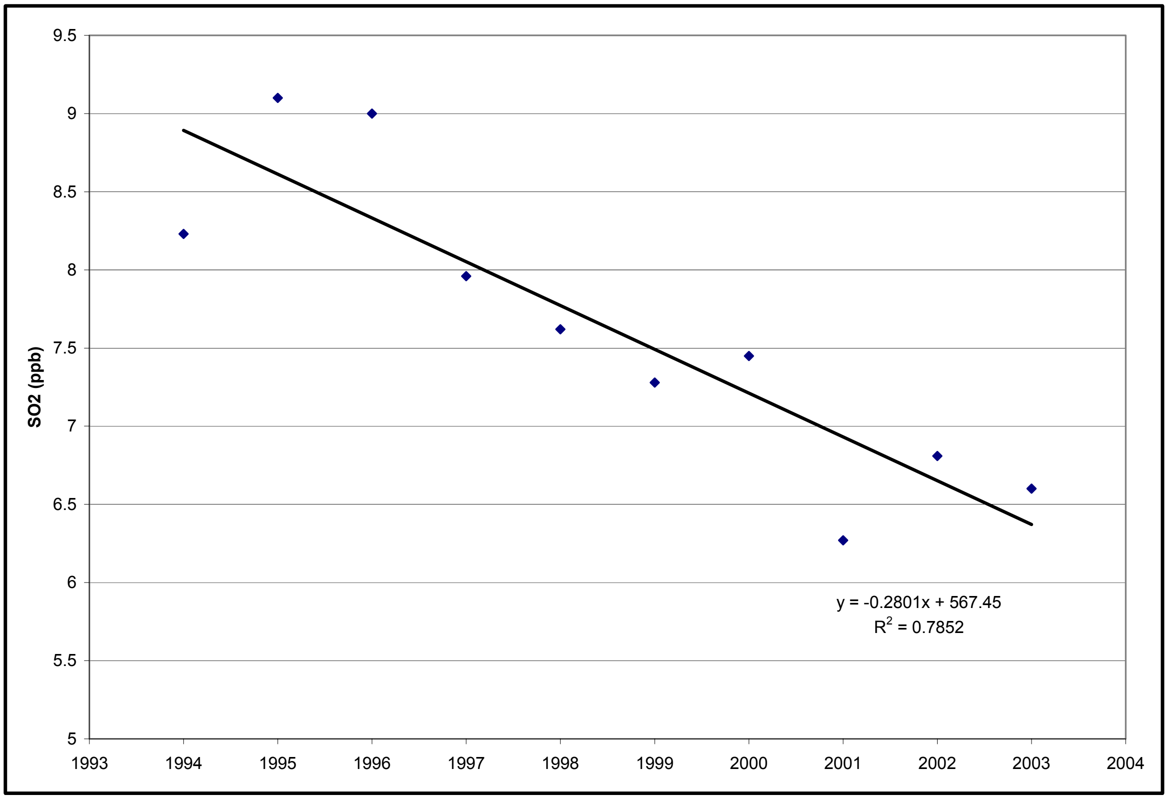
	pH (SU)
Minimum	3.69
1st quartile	4.45
Median	4.64
3rd quartile	4.89
Maximum	7.95
Mean	4.74

Source: National Atmospheric Deposition Program

The primary anthropogenic source of acid rain is sulfur dioxide, of which Doe Run's Glover Smelter was the principle source in the vicinity of McKenzie Creek. The smelter is located about 17 miles north of the GS Roofing facility. It ceased operation in December 2003 and it is possible that this event may help to mitigate the acid rain problem (McGee, 2004). Over the last ten years of operation, there has been a steady decline in the annual average of sulfur dioxide detected from this facility (Figure 2).

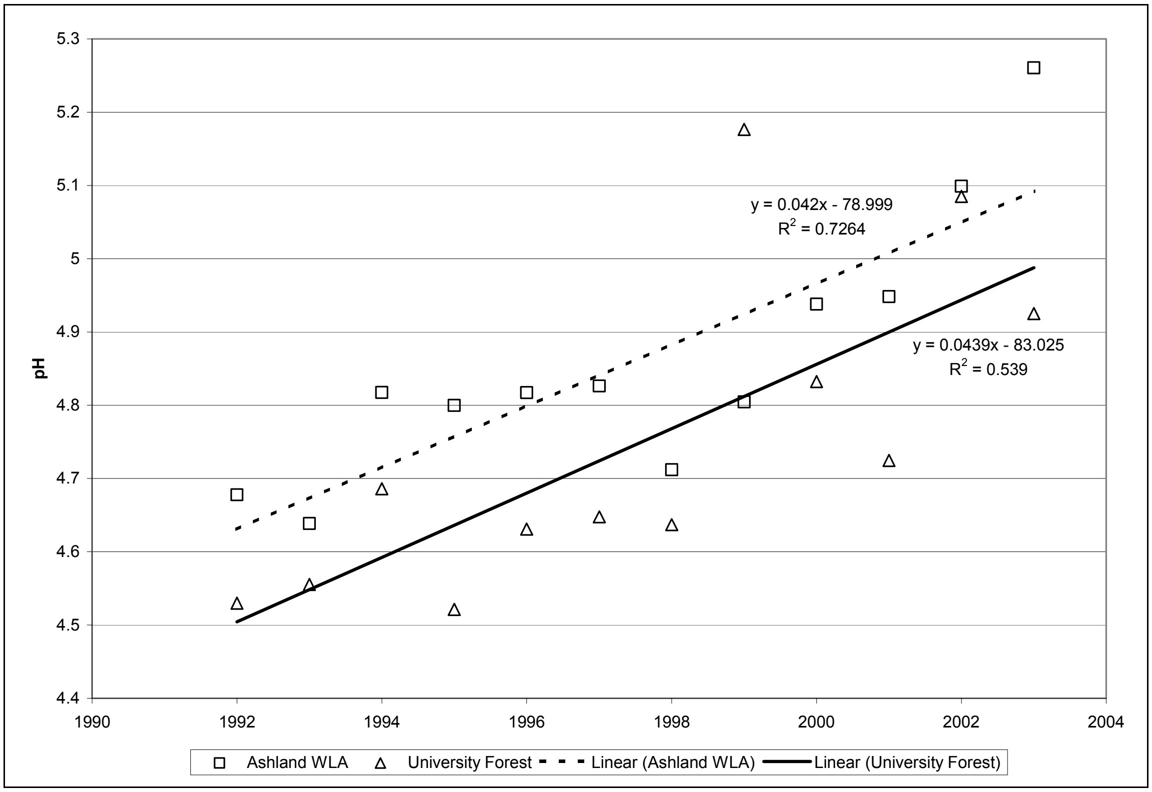
Sulfur dioxide emissions are produced primarily through the sintering process, in which sulfur compounds are separated from the lead containing minerals with a blast of hot air. The Glover smelter was constructed prior to the federal Clean Air Act, and therefore was not required to obtain an air pollution construction permit or to control emissions of sulfur dioxide (Rustige, 2004).

Figure 1: Average annual ambient detection of sulfur dioxide near Glover Smelter



Over the last ten years, there has been a trend toward more neutral pH in the precipitation measured at University Forest. This is consistent with the nationwide trend of generally reduced acidity in precipitation that is attributed to reduced sulfur dioxide emissions (Nilles 2003). Figure 2 shows a comparison of the trend at University Forest with that of the Ashland Wildlife Area, located 120 miles to the northwest of the smelter. The Ashland Wildlife Area, usually upwind from the Glover facility, has for the most part had slightly higher pH in its precipitation. A more detailed analysis comparing the local rainfall acidity with background acidity is in Appendix D.

Figure 2: Trends in average annual precipitation pH at University Forest and Ashland Wildlife Area



Buffering Capacity

In most Missouri streams the acidity of rainfall is quickly buffered by the calcium carbonate which comes from an abundance of carbonate rocks (limestone and dolomite) in stream bottoms and within watersheds. As a result, stream water in most of the State is generally neutral or slightly alkaline. However, McKenzie Creek is located in the St. Francois Mountains, where the prevailing geology includes a relatively small proportion of limestone. Surface formations in the vicinity of McKenzie Creek include the St. Francois Mountains Volcanic Subgroup, consisting mainly of granite and rhyolite, and the upper Cambrian formations, which have a prevalence of dolomite (Thompson, 1995).

Granite and rhyolite are silicate based rock types that do not provide buffering capacity to solutions that come in contact with them. In this environment, the capacity of streams to neutralize acidity is reduced, particularly in headwater areas (Winter et al, 2002). The portion of McKenzie Creek upstream from the impaired segment is predominantly underlain by rhyolite. The downstream segment is underlain by a greater presence of dolomite, which has buffering capacity (McGee, 2004).

Another potential source for natural acidity in the stream is the soil adjacent to the stream. In the area of the impaired segment, McKenzie Creek flows through a narrow flood plain of soil with acidic characteristics. This area has been mapped as the Tilk-Secesh complex. The Tilk series is a loamy-skeletal, siliceous, active, mesic Ultic Hapludalf. Its reaction ranges from strongly acidic to slightly acidic in the surface horizon, and very strongly acidic to moderately acidic in the

subsurface. The Secesh series is a fine-loamy, siliceous, active, mesic Ultic Hapludalf. It is strongly acidic to slightly acidic at the surface, and very strongly acidic to moderately acidic in the subsurface (USDA-NRCS, 2004).

Further downstream, where water samples yielded more neutral pH, the soil in the flood plain has somewhat less acidic characteristics. The area is mapped as the Relfe-Sandbur complex. The Relfe series is a sandy-skeletal, siliceous, mesic Mollic Udifluvent. Surface reaction is strongly acidic to neutral and the subsurface ranges from moderately acidic to neutral. The Sandbur series is a coarse-loamy, siliceous, superactive, nonacidic, mesic Mollic Udifluvent. Both the surface and subsurface are moderately acidic to neutral (USDA-NRCS, 2004).

2. Description of the Applicable Water Quality Standards and Numeric Water Quality Targets

Designated Uses

The designated uses of McKenzie Creek, WBID 2787, are:

- Livestock and Wildlife Watering
- Protection of Warm Water Aquatic Life
- Protection of Human Health associated with Fish Consumption

The use that is impaired is Protection of Warm Water Aquatic Life. The stream classifications and designated uses may be found at 10 CSR20-7.031 (1)(C) and Table G.

Anti-degradation Policy

Missouri's Water Quality Standards include the Environmental Protection Agency (EPA) "three-tiered" approach to anti-degradation, and may be found at 10 CSR 20-7.031(2).

Tier 1 – Protects existing uses and provides the absolute floor of water quality for all waters of the United States. Existing instream water uses are those uses that were attained on or after November 29, 1975, the date of EPA's first Water Quality Standards Regulation, or uses for which existing water quality is suitable unless prevented by physical problems such as substrate or flow.

Tier 2 – Protects the level of water quality necessary to support propagation of fish, shellfish, and wildlife and recreation in and on the water in waters that are currently of higher quality than required to support these uses. Before water quality in Tier 2 waters can be lowered, there must be an antidegradation review consisting of: (1) a finding that it is necessary to accommodate important economical or social development in the area where the waters are located; (2) full satisfaction of all intergovernmental coordination and public participation provisions; and (3) assurance that the highest statutory and regulatory requirements for point sources and best management practices for nonpoint sources are achieved. Furthermore, water quality may not be lowered to less than the level necessary to fully protect the "fishable/swimmable" uses and other existing uses.

Tier 3 – Protects the quality of outstanding national resources, such as waters of national and State parks and wildlife refuges and water of exceptional recreational or ecological significance. There may be no new or increased discharges to these waters and no new or increased discharges to tributaries of these waters that would result in lower water quality (with the exception of some limited activities that result in temporary and short-term changes in water quality).

Specific Criteria
Missouri's Water Quality Standards (WQS), 10 CSR20-7.031 Section (4)(E), state that water contaminants shall not cause pH to be outside of the range of 6.5-9.0 Standard Units (SU).

3. Calculation of Load Capacity

Load capacity (LC) is defined as the greatest amount of a pollutant a waterbody can assimilate without being in violation of Missouri's Water Quality Standards. This total load is then divided among a Waste Load Allocation (WLA) for point sources, a Load Allocation (LA) for nonpoint sources and a margin of safety (MOS). Unlike other pollutants, pH is not a load in the conventional sense. Rather, it is a measure of the acidity or alkalinity of a solution (Webnox. 2003). More precisely, it is defined as the negative logarithm (base 10) of the hydrogen ion concentration in solution. This is how the Standard Units of pH are derived. A solution with a neutral pH of 7 has a concentration of 10^{-7} gram-atoms of hydrogen ions per liter, and is one tenth as acidic as a solution with a pH of 6, that has a concentration of 10^{-6} gram atoms of hydrogen ions per liter.

Hydrogen ions are a very changeable component of water quality. When introduced to a solution with common buffers such as calcium carbonate, they react quickly to produce carbonic acid, which then degrades to produce water and carbon dioxide.

Therefore, rather than a mass-per-unit time measure, this TMDL uses a different appropriate measure, as allowed by 40CFR §130.2(i). In this case, it is the Missouri state water quality criteria of a range between 6.5 and 9 SU (the State Water Quality Standard).

4. Load Allocation (Nonpoint Source Load)

Load Allocation (LA) is the maximum allowable amount of the pollutant that can be assigned to nonpoint sources. In consideration of the local geology, soil and precipitation characteristics, it is evident that land use management within the watershed will have a limited impact in controlling acidity in the stream. Application of lime on crops and pasture lands may help mitigate stream acidity on a temporary basis, but such amendment is economically unfeasible and it would affect a relatively small portion of the watershed.

The principal nonpoint source of acidity is unbuffered acid rain that is partially attributable to sulfur dioxide emissions from the Glover Smelter. Background atmospheric contributions include sulfur dioxide drifting from more distant sources as well as the natural production of carbonic acid from carbon dioxide. The Glover Smelter halted operations in December 2003 because of economic reasons. Previously, it was emitting SO_x (all types of sulfur oxides) at rates between 20,000 and 50,000 tons per year. Because this is an older facility, there are no real controls on SO_x emissions.

The LA for this TMDL prescribes that runoff will achieve a pH of 6.5 to 9. The Glover Smelter shutdown and unspecified reductions in sulfur dioxide (SO_2) air emissions may have already resulted in this LA. Future monitoring will track the goal.

5. Waste Load Allocation (Point Source Loads)

The Wasteload Allocation (WLA) is the maximum allowable amount of the pollutant that can be assigned to point sources. As already stated, the only permitted point source within the watershed

upstream from the impaired segment is Gad's Hill Quarry, which is managed by GS Roofing Company. The current permit requires the effluent pH be maintained in the range of 6.0 to 9.0, which conforms to the effluent regulations [at 10 CSR 20-7.015(8)(B) 2]; this existing permit expires October 4, 2006. As characterized in the source analysis section, and in reviewing the data from McKenzie Creek in Appendix C, the extent of the impact of the quarry discharge on McKenzie Creek is not clear at this time. Requiring the quarry to increase pH by 0.5 SU, without further monitoring data that shows this to be a necessary action which will improve water quality, is not justified at this time. This is a phased TMDL and as Phase I, the quarry will provide the department with pH data on a monthly basis both from the outfalls and also from several points in McKenzie Creek as listed in Table 2 through the life of their existing permit.

Table 2: Sampling Site Locations

Site #	Site ID	Latitude	Longitude	Description
1	2787/3.7	37.23640	-90.71410	McKenzie Cr. Hwy CC, SWNW Sec.34, 30N,3E
2	2787/3.65/.1	37.23580	-90.71410	Trib. From Gads Hill Quarry @NESW Sec.34, 30N,3E
3	2787/3	37.22610	-90.71480	McKenzie Cr. Hwy 49 bridge, NWNW Sec.3,29N,3E
4	2787/1.5	37.19790	-90.70760	McKenzie Cr. @ county road, SWSE Sec.10,29N,3E

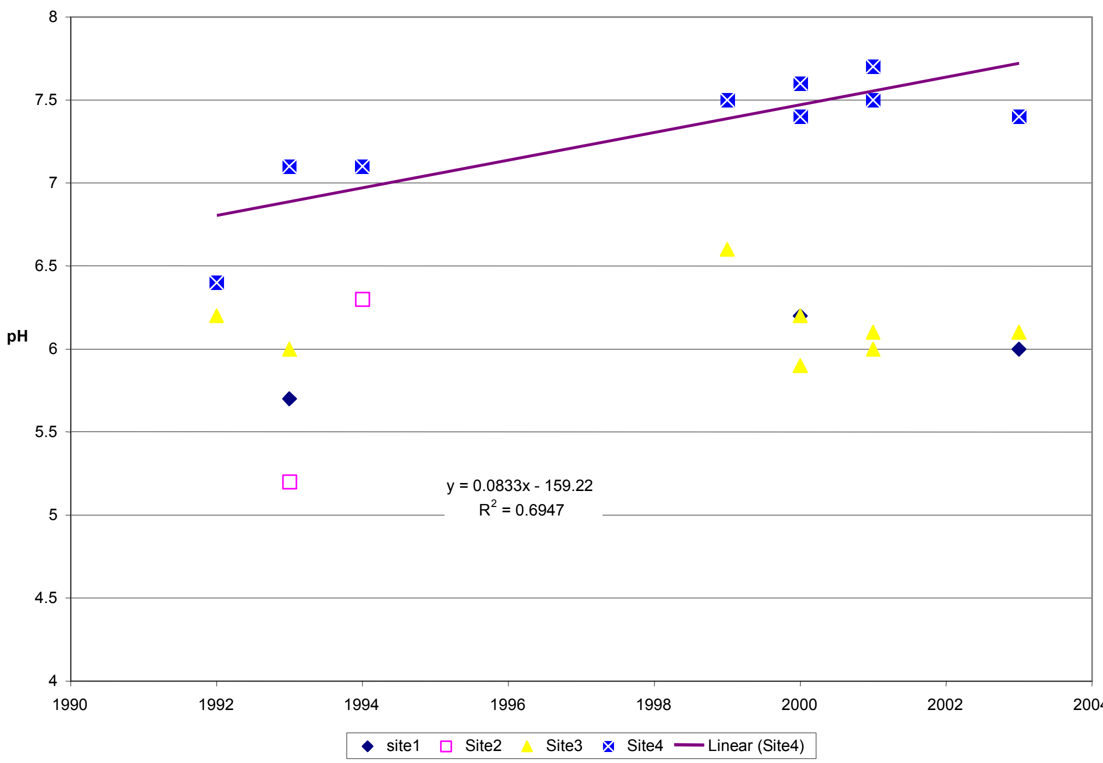
This information should confirm whether or not the quarry is contributing to acidity in McKenzie Creek; this information will also be compared to temporal trends anticipated in decreasing the acid deposition load of the Glover Smelter facility due to the shutdown of that facility in December 2003. If the monitoring data indicates the quarry discharge is contributing to the problem, Phase II of this TMDL will dictate a revised pH limit for inclusion in the quarry's re-issued NPDES permit with an appropriate compliance schedule that will ensure WQS will be met.

Since the pH cannot be expressed as a load, for the purposes of Phase I of this TMDL, the WLA for this TMDL will be no deviation from the current pH limits of 6.0 to 9.0 S.U. in the quarry's NPDES permit.

6. Margin of Safety (MOS)

The margin of safety is used to account for uncertainty concerning the relationship between pollutant load and instream water quality, and for this TMDL is implicit based upon the following conservative assumptions. Any new discharger that may locate in the watershed will have to meet the pH water quality standard at end of pipe. Glover Smelter closed December 2003, as previously stated; if the Doe Run Corporation decides to resume operations, the smelter will need to have more stringent air emission limits than it had historically. This will help to ensure protection of water quality as well as air quality in the watershed. The yearly average pH value at Site 4 (Figure 4) follows an increasing linear trend and all individual samples have been consistently above 7 since 1993 (graph below).

Figure 4: Instream pH in McKenzie Creek



7. Seasonal Variation

While it is acknowledged that the pH of any given water sample varies with temperature, the WQS of 6.5 - 9.0 SU applies year-round.

8. Monitoring Plans for TMDL under the Phased Approach

Fiscal year 2005 quality assurance project plan (FY05 QAPP) calls for monitoring three times a year in the upper McKenzie Creek at the four sites in Table 2. The parameters include pH, Alkalinity, Dissolved Oxygen, Sulfate, Specific Conductivity, and a suite of others less relevant to this TMDL. Now, GS Roofing will also be monitoring pH at the same four locations.

9. Implementation

The acidity of the local precipitation and in the flood plain soils, as well as reported acidity in water from springs upstream of the impaired segment, are indicative that much of the acidification in McKenzie Creek is due to factors that are beyond the control of the only point source discharger in the watershed, GS Roofing. There are also no readily identifiable practices that would mitigate the nonpoint sources of acidity.

If the Doe Run Corporation at any time chooses to resume operations at the Glover smelter, air quality modeling will need to be done to demonstrate compliance with the National Ambient Air Quality Standard for sulfur dioxide. To meet the standard, SO_2 emissions will likely need to be

reduced from historic emission rates. These emission reductions, in turn, will help to protect McKenzie Creek and other streams in the St. Francois Mountains from the effects of acid rain. Continued improvements in air quality through SO_2 control are likely to improve pH values in McKenzie Creek.

All Missouri TMDLs are phased. If future monitoring reports reveal that water quality standards are not being met, this TMDL will be re-opened and re-evaluated.

10. Reasonable Assurances

Should the Glover Smelter resume operations after December 1, 2008 (five years from shut-down), the department's Air Pollution Control Program will have the authority to write and enforce permits establishing more stringent SO_2 emission limits. Compliance with such limits enforced through monitoring and monthly reports should provide reasonable assurance that air quality will improve with a corresponding improvement in water quality. Parallel changes in 10 CSR 10-6.260 *Restriction of Emission of Sulfur Compounds*, which establishes specific SO_2 emission limits, will also be necessary. If the Glover Smelter does resume operation prior to December 1, 2008, they must comply with 10 CSR 10-6.260. The regulation prohibits SOx sources from causing or contributing to violations of the National Ambient Air Quality Standard, which will need to be demonstrated through an air quality modeling study prior to start-up.

11. Public Participation

This water quality limited segment is included on the approved 2002 303(d) list for Missouri. The Missouri Department of Natural Resources, Water Protection Program, developed this TMDL. The public notice period was from June 4 to July 4, 2004. Groups receiving the public notice announcement included the Missouri Clean Water Commission, the Water Quality Coordinating Committee, the TMDL Policy Advisory Committee, Stream Team volunteers in the watershed (50), the appropriate legislators (4), GS Roofing Company and others that routinely receive the public notice of Missouri State Operating Permits. A copy of the notice, any comments received and the department responses will be placed in the McKenzie Creek file.

12. Appendices and List of Documents on File with the department

Appendix A – Land Use Map for the McKenzie Creek Watershed
Appendix B – Map of Sample Locations and Impaired Stream Segment
Appendix C – Water Quality Data for McKenzie Creek
Appendix D – Comparative Analysis of Acid Precipitation

Documents on File

GS Roofing Company, Permit #MO-0110051

Precipitation and pH data from the National Atmospheric Deposition Program, National Trends Network, collected at the University Forest monitoring station and the Ashland Wildlife Area in Missouri and at Buffalo Point, Arkansas

McKenzie Creek Information Sheet

Public Notice announcement

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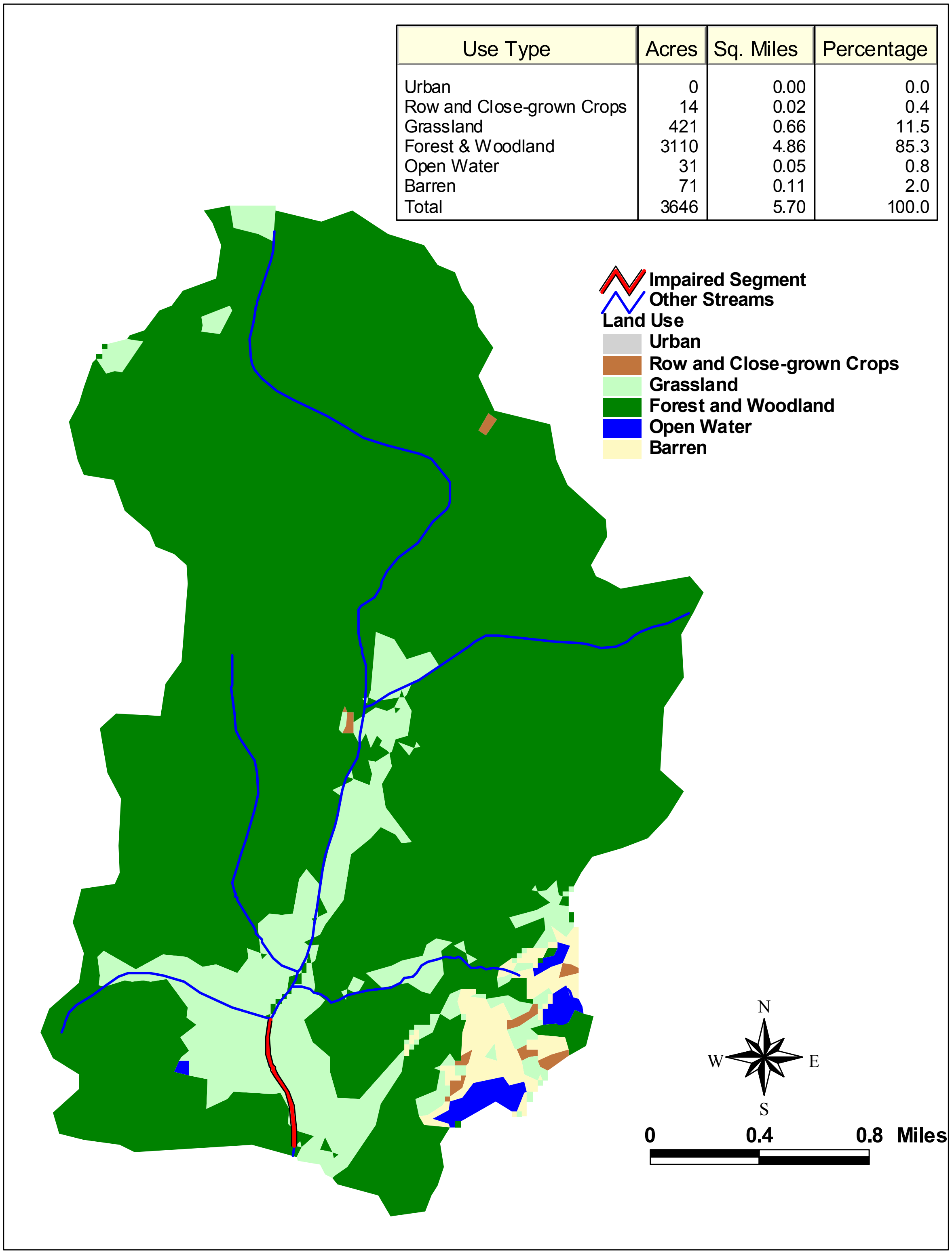
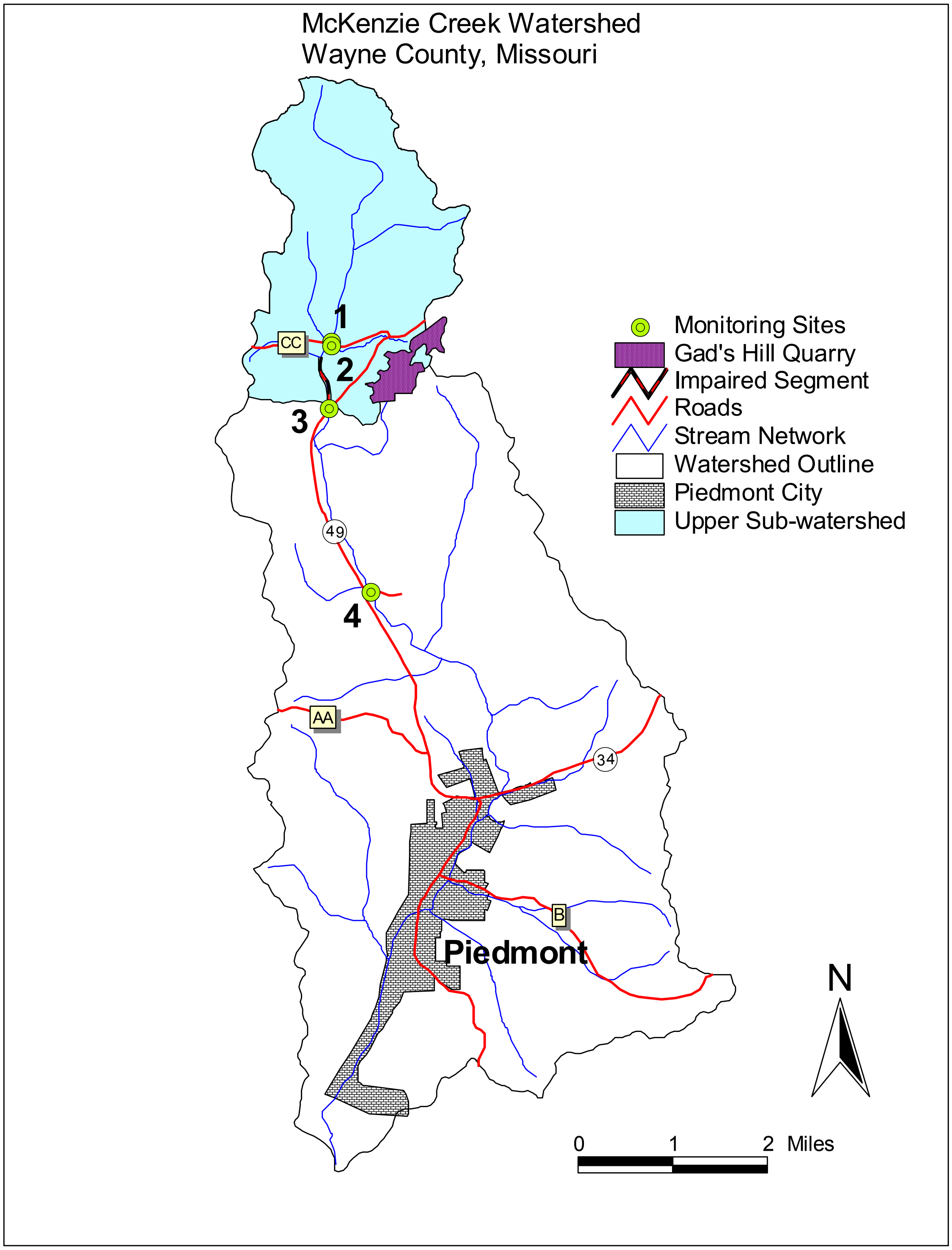
Appendix A
Land Use Map for McKenzie Creek



Use Type	Acres	Sq. Miles	Percentage
Urban	0	0.00	0.0
Row and Close-grown Crops	14	0.02	0.4
Grassland	421	0.66	11.5
Forest & Woodland	3110	4.86	85.3
Open Water	31	0.05	0.8
Barren	71	0.11	2.0
Total	3646	5.70	100.0

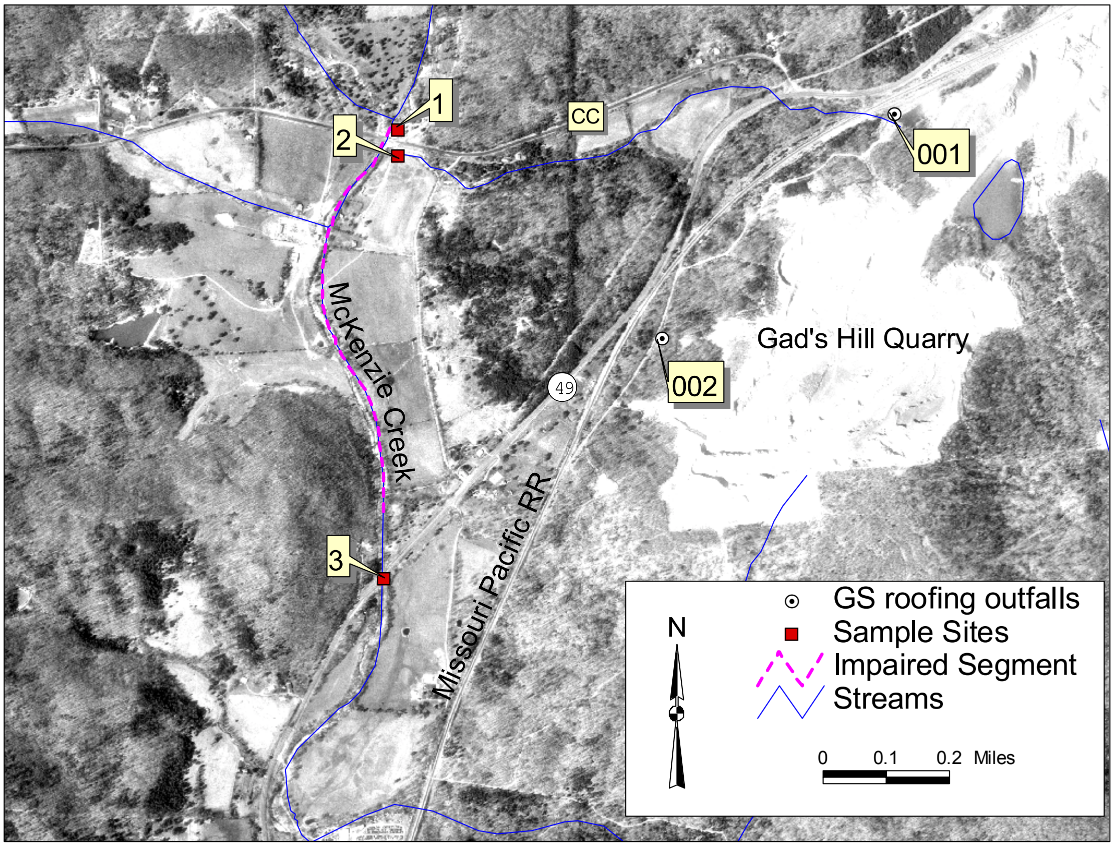
Appendix B-1
Sample Locations and the Impaired Segment of McKenzie Creek



Site Index

1 – McKenzie Creek 0.1 mile above Quarry tributary
2 – Tributary from Gad's Hill Quarry near mouth
3 – McKenzie Creek 2 miles below Gad's Hill Quarry
4 – McKenzie Creek 3.5 miles below Gad's Hill Quarry

Appendix B-2
Quarry Outfall Locations in Spatial Relation to the Monitoring Sites



Appendix C
Water Quality Data for McKenzie Creek

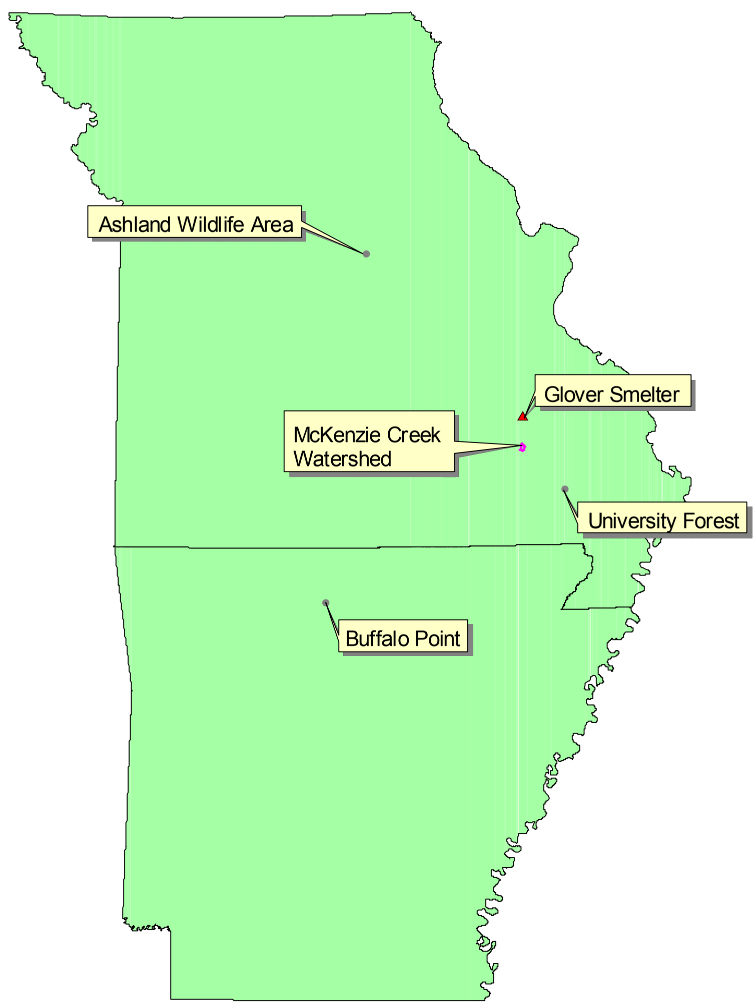
Site #	Site Name	Date	Flow	^oC	pH	SC	Alk
1	McKenzie Cr. 0.1 mi.ab. Quarry trib.	9/16/1993			5.7		
1	McKenzie Cr. 0.1 mi.ab. Quarry trib.	4/6/2000	0.25	18	6.2	32	
1	McKenzie Cr. 0.1 mi.ab. Quarry trib.	7/16/2003		26	6	100	9
2	trib.from Gad's Hill quarry nr.mouth	9/16/1993	0.02		5.2		
2	trib.from Gad's Hill quarry nr.mouth	4/15/1994			6.3	180	
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	10/15/1992	0.15		6.2	180	
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	9/16/1993	0.25		6		
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	8/31/1999	0		6.6	187	
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	4/6/2000	0.3	19	6.2	141	
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	5/18/2000	0.01	19	5.9	157	
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	8/24/2000	0.02		5.9	334	
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	6/19/2001	0.15	21	6	488	10
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	7/18/2001	0.1	23	6.1	525	20
3	McKenzie Cr. 2 mi.bl. Gad's Hill quarry	7/16/2003		23	6.1	242	17
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	10/15/1992	0.4		6.4	160	
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	9/16/1993			7.1		
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	4/15/1994			7.1	80	
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	8/31/1999	0.1		7.5	206	
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	4/6/2000	0.9	18	7.6	154	
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	5/18/2000	0.15	20	7.4	196	
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	8/24/2000	0.15	23	7.6	238	
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	6/19/2001	0.2	23	7.5	230	77
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	7/18/2001	0.2	24	7.7	247	85
4	McKenzie Cr. 3.5 mi.bl. Gad's Hill quarry	7/16/2003		23	7.4	223	79

Abbreviations and units of measurement:
Cr.=Creek; mi.=mile; ab.=above; trib.=tributary; nr.=near; bl.=below
Flow is reported in cfs; ^0C=Temperature in degrees Celsius; pH in SU; SC=Specific Conductivity in µS/cm;
Alk=Alkalinity in mg/L

Appendix D
Comparative analysis of acid precipitation

To determine whether the rainfall acidity is primarily due to sulfur dioxide emissions from the Glover Smelter, or more because of background factors, a comparison was made between the precipitation data for the University Forest station and two reference stations that are located in the region but at a greater distance from the smelter. Weekly precipitation pH data from 1991 to 2003 were drawn from monitoring stations in the Ashland Wildlife Area in Boone County, Missouri, and at Buffalo Point in Marion County, Arkansas. These data were compared on a temporal basis with equivalent data from the University Forest station, in Butler County, Missouri.

Figure D-1: Location of the Monitoring Stations



There are two assumptions in this comparison. One is that for those weeks in which there are data for the University Forest station and either or both of the reference stations, the precipitation is from events occurring in similar general weather patterns. The other is that the reference stations are

both usually upwind from Glover Smelter. During the relatively infrequent times that the wind is from the east, the stations are at sufficient distance that precipitation acidity resulting from smelter emissions would be dispersed.

Weekly pH readings for the University Forest monitoring station were subtracted from readings for the same week at both of the reference stations. A positive result indicated greater acidity at the University Forest station, and a negative result indicated the opposite. Tied readings were counted as zero and discarded. The large sample size made it possible to use a large sample approximation to modify the data set to a normal distribution. The probability of results were derived as follows (Helsel and Hirsch, 2002):

$$Z^+ = [S^+ - ½ - \mu_{S+}] / \sigma_{S+}$$

where

Z^+ = Number of standard deviations above 0 in a normal distribution.
S^+ = Number of positive results.
n = Number of comparisons
μ_{S+} = n/2
$\sigma_{S+} = ½ \sqrt{n}$

Results were as follows:

pH comparison	Buffalo Point – University Forest	Ashland Wildlife Area – University Forest
n	301	267
S^+	172	150
μ_{S+}	150.5	133.5
σ_{S+}	17.349	8.17
Z^+	1.21	1.96

Note: The data used in this comparison are not included in this document, but are on file with the department and are available on request.

For each comparison, the null hypothesis is that there is no significant difference in the pH of precipitation between what is monitored at the University Forest station and at the reference station. If the normal procedures for determining probability are applied, and if $\alpha = 0.05$, then the null hypothesis is accepted for the Buffalo Point - University Forest comparison, and rejected for the Ashland Wildlife Area - University Forest comparison. Given that there are a large number of unspecified variables that influence precipitation pH at any given time, a larger α value may be appropriate. The probability of exceeding 1.21 standard deviations above the mean which is indicated for the Buffalo Point - University Forest comparison is about 12 percent (Adams, 2003).